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Biodegradation of Sorbed Chemicals in Soil

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Rates of biodegradation of sorbed chemicals are usually lower in soil than in aqueous systems, in part because sorption reduces the availability of the chemical to microorganisms. Biodegradation, sorption, and diffusion occur simultaneously and are tightly coupled. In soil, the rate of biodegradation is a function of a chemical's diffusion coefficient, sorption partition coefficient, the distance it must diffuse from the site of sorption to microbial populations that can degrade it, and its biodegradation rate constant. A model (DSB model) was developed that describes biodegradation of chemicals limited in the availability by sorption and diffusion. Different kinetics expressions describe biodegradation depending on whether the reaction is controlled by mass transfer (diffusion and sorption) or the intrinsic biodegradation rate, and whether biodegradation begins during or after the majority of sorption has occurred. We tested the hypothesis that there is a direct relationship between how strongly a chemical is sorbed and the chemical's biodegradation rate. In six soils with different organic carbon contents, there was no relationship between the extent or rate of biodegradation and the sorption partition coefficient for phenanthrene. Aging of phenanthrene residues in soil led to a substantial reduction in the rate of biodegradation compared to biodegradation rates of recently added phenanthrene. Considerable research has focused on identification and development of techniques for enhancing *in situ* biodegradation of sorbed chemicals. Development of such techniques, especially those involving inoculation with microbial strains, should consider physical mass transfer limitations and potential decreases in bioavailability over time. — Environ Health Perspect 103(Suppl 5):93–95 (1995)

Key words: biodegradation, sorption, phenanthrene, aging, bioavailability

Sorbed chemicals present one of our most challenging environmental problems in the bioremediation of contaminated soils and sediments. Rates of biodegradation of sorbed chemicals are lower than in aqueous systems or laboratory cultures, in part because sorption reduces the availability of the chemical to soil microorganisms. Our understanding of the biodegradation of sorbed chemicals is confounded by the fact that the term sorption is often used to describe different interactions between pollutants and the soil matrix. These interactions include different mechanisms of adsorption, diffusion, bound residue formation and aging of residues. Multiple processes may affect the same chemical and, in soil, it is difficult to isolate one process from another. It is crucial to the future success of bioremediation that research continues on the physical and chemical aspects of pollutant–soil interactions and their impact of biodegradation.

Adsorption is the specific term for the condensation of vapors or solutes on surfaces or pores of a solid by physical or chemical bonding forces. Different types of sorption processes include hydrophobic sorption (or partitioning), van der Waals–London interactions, charge-transfer (e.g., hydrogen bonding), ligand exchange, and ion exchange reactions. Because many environmental pollutants are nonionic and nonpolar, the emphasis of this study is on hydrophobic associations with soil organic matter.

The sorption partition coefficient, K_d or K_{oc}, describes the affinity of a chemical for a sorbent. Assumptions for using the K_d relationship are that organic matter is the sorbent; there are no specific reactions between sorbent and chemical; sorption is instantaneous, reaches an equilibrium, and is reversible, and the sorption isotherm is linear. In reality, however, some chemicals (e.g., many pesticides) have polar functional groups that may form chemical bonds with soil organic matter. Clay may contribute to sorption, particularly in surface soils with low organic matter contents and in subsurface material. Organic matter may differ in its quality and ability to sorb. Over time, K_d values often increase due to formation of bound or aged residues. Bound residues result from the formation of covalent bonds between a pollutant and organic matter. Aging is a commonly observed, yet poorly understood, field phenomenon in which a pollutant becomes increasingly difficult to extract from soil over time. Both of these processes, unlike sorption, lead to apparently irreversible associations between the pollutant and soil. Finally, sorption in soil is usually a nonequilibrium process because the rate of both adsorption and desorption is limited by diffusion of the chemical between the solution and sorbed phase. In fact, sorption and diffusion are inseparable processes in soils at field moisture levels, though perhaps less so in soil slurries or suspended sediments.

To help interpret the effects of sorption/desorption and diffusion on the metabolism of organic chemicals, a mathematical model (DSB model) was developed to describe biodegradation in substrate-limited systems (*1*). The model assumes diffusion is described by Fick's second law, sorption by a linear isotherm, and biodegradation by any of various rate equations that can be derived from the Monod equation, including first-order kinetics. Other assumptions are that only the solution phase of the chemical is used, microorganisms are excluded from inside the aggregates, sorption is instantaneous once the chemical diffuses to the sorption

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site, and there is no surface diffusion. The assumption that the sorbed phase cannot be used by microorganisms is debatable and requires additional research. However, on an aggregate scale, most aerobic organisms and activity appear to be associated with the outer layers, and populations in inner regions are limited by diffusion of substrate, nutrients, and oxygen.

Model simulations were compared to experimental data measured in several well-defined experimental systems (*2*). Using physical and biological measurements from the systems as input parameters, the simulations were similar to measured data describing biodegradation of phenol by a pure culture of *Pseudomonas* sp. in the presence of kiln-fired clay aggregates, as well as in other well-defined systems.

Sensitivity analyses were performed using the DSB model to determine the dependence of a chemical's apparent half-life on physical and chemical properties of soil (*3*). In soil, the rate of biodegradation is a function of a chemical's diffusion coefficient, sorption partition coefficient, the distance it must diffuse from the site of sorption to microbial populations that can degrade it, and its biodegradation rate constant. Different kinetic expressions describe biodegradation over time depending on whether the reaction is controlled by mass transfer (diffusion and sorption) or the biological rate and whether the chemical starts out as sorbed (inside the aggregate) or not sorbed (in the outside solution) (Figure 1). The ϕ depicted on the graphs is a dimensionless term consisting of the diffusivity (D_e), the biodegradation rate constant (k), aggregate radius (R), adsorption capacity (K), and porosity (e) and is expressed as:

$$\phi = \sqrt{\frac{R\{\varepsilon + K(1-\varepsilon)\}k}{D_e}} \quad [1]$$

Thus an increase in ϕ can result from an increase in the sorption partition coefficient or aggregate radius or from a decrease in the diffusion coefficient. If biodegradation is rapid relative to the mass transfer rate ($\eta = 0.1$), there is little impact of sorption on the rate of degradation of a chemical starting out in the solution phase; however, sorption is more important if the chemical is already sorbed. For chemicals starting out in solution and with slower degradation rates relative to the mass transfer rate ($\eta = 1.0$), initially there is a brief and rapid rate of biodegradation of the chemical available in solution. Once most of the solution concentration has been depleted by biodegradation or diffusion into the aggregate, there is a much slower rate of biodegradation controlled by mass transfer of the chemical back out of the aggregate. When the chemical starts out sorbed, an increase in the sorption partition coefficient changes the kinetics of biodegradation from first order to zero order within the simulated time. Considering that many organic pollutants sorb strongly and numerous soils have some degree of aggregation and organic matter, taking into account the physical and chemical processes affecting a chemical's concentration may improve mathematical models of the kinetics of biodegradation in soil.

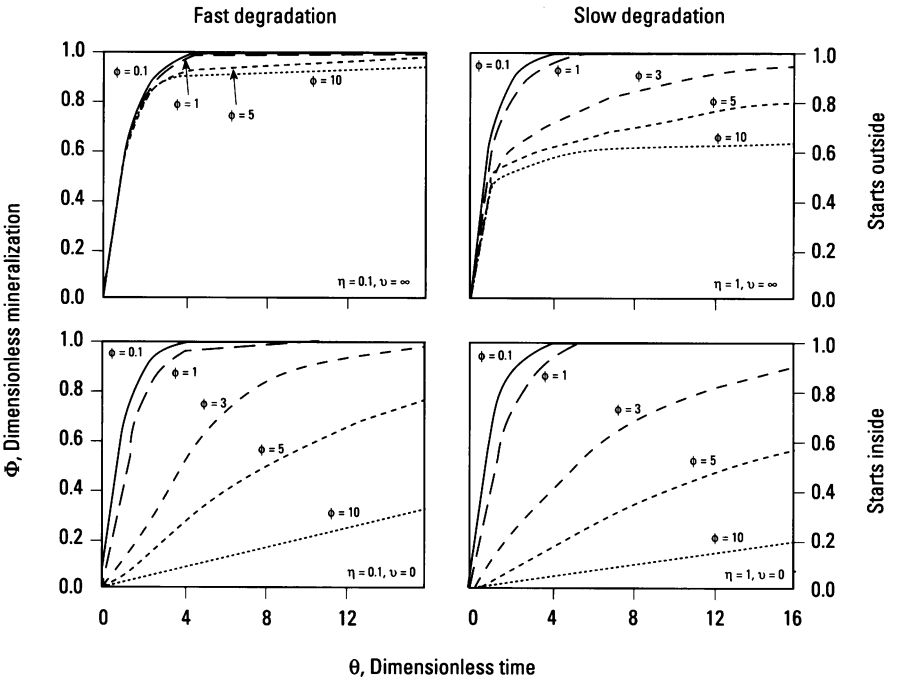

Figure 1. Simulations of the biodegradation of a chemical limited in availability by diffusion and sorption. Adapted from Chung et al. (*3*).

Model predictions and measured data were compared for several experiments conducted in soil or soil slurries. The model compared well with data depicting biodegradation of a low concentration of *para*-nitrophenol by indigenous microbial populations in soil amended with artificial sorbent, in this case hydrophobic chromatography beads. Increasing the ratio of solution to soil resulted in higher rates of degradation of phenanthrene by soil populations; the model showed similar trends.

Experiments were conducted to determine if there is a relationship between sorption and biodegradation in different soils varying in their organic matter content. A preliminary study had suggested a relationship between biodegradation rate and the measured K_{oc} for several soils. The biodegradation of a low concentration (50 ng/g) of phenanthrene was measured in soils with organic carbon (OC) contents ranging from 3.6 to 9.5%. A low concentration was selected to minimize the influence of growth on phenanthrene biodegradation kinetics, and high organic matter soils were selected to ensure substantial sorption of the chemical. The rates of biodegradation varied by soil type (Figure 2), with the highest rate observed in the soil with the highest OC content. Measured K_d values for phenanthrene in the six soils varied by a factor of 10, whereas K_{oc} values varied by a factor of two (Table 1). Desorption isotherms showed that the sorption of phenanthrene was partially irreversible. Linear regression analysis showed no relationship between the biodegradation rate and either K_{oc} or K_d for the soils tested.

It becomes increasingly difficult to extract chemicals the longer they have been in contact with soil. The decreased extractability (aging) is associated with a decrease in the bioavailability and degradability of the chemicals. The phenomenon

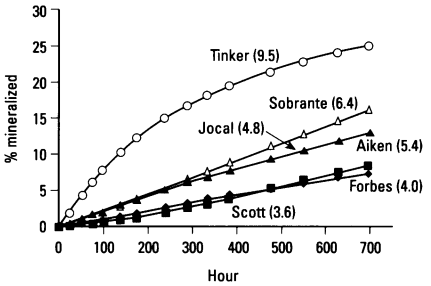

Figure 2. Phenanthrene degradation in high organic matter soils (% organic carbon).

Table 1. Sorption partition coefficients for various soils.

Soil	Organic carbon, %	K_d	K_{oc}
Scott	3.60	816	22,671
Forbes	3.94	841	21,339
Jocal	4.78	852	17,822
Aiken	5.38	968	17,991
Sobrante	6.41	733	11,431
Tinker	9.47	2041	21,555

of aging has been observed for ethylene dibromide (*4*) and other volatile chemicals. The rate of biodegradation of phenanthrene by a pure culture of *Arthrobacter oxidans* incubated in sterile soil under unsaturated conditions was substantially reduced relative to the rate in freshly amended soil, regardless of whether incubations were done under saturated conditions or in soil suspensions (Figure 3).

New methods are needed to study the biodegradation of sorbed pollutants in soil because existing approaches, such as use of soil slurries, may significantly alter soil properties (e.g., available carbon, access to sorption sites), may decrease the time needed for sorption to reach equilibrium, and do not represent field conditions. Especially needed are noninvasive techniques that preserve the physical distribution of microorganisms and pollutants in soil and do not destroy soil structure.

In conclusion, many pollutants assumed to be sorbed to soil may also have irreversible or partially reversible interactions with soil particles, or their availability to microorganisms may be limited by diffusion rather than purely desorption. Theory developed for simple sorption may not be applicable to many bioremediation conditions. There are many exciting research questions to explore: What are the different mechanisms involved in pollutant–soil interactions and do they differ in their impact on bioavailability? What is the spatial distribution of sorbed pollutants and microbial populations in the soil matrix? What specific properties of microorganisms (e.g., surfactant production, ability to attach, ability to use the sorbed phase directly) might enhance the degradation of sorbed pollutants? To enhance *in situ* biodegradation rates, what physical treatments of soil at field moisture levels increase bioavailability without adversely affecting microbial populations?

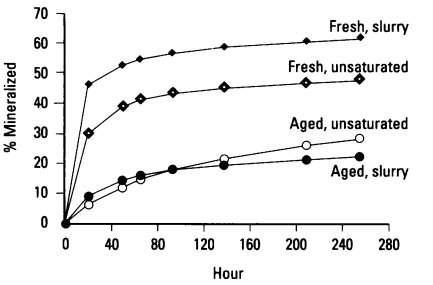

Figure 3. Effect of aging on phenanthrene biodegradation in Yolo soil.

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